KINETICS, CATALYSIS, AND REACTION ENGINEERING

Liquid-Phase Oxidation of Carvacrol Using Zeolite-Encapsulated Metal Complexes

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We report here the use of zeolite-encapsulated metal (salpn) complexes as catalysts in the oxidation reaction of the natural compound carvacrol in acetonitrile with hydrogen peroxide as the oxidant. No previous studies on the oxidation of carvacrol in the presence of metal salpn complexes have been reported. By using a general flexible ligand method, Cr(III), Fe(III), Bi(III), Ni(II), and Zn(II) complexes of *N,N'*-bis(salicylidene)propane-1,3-diamine (H₂salpn) encapsulated in NaY zeolite were prepared. All catalysts were characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM) analyses to confirm the complex encapsulation. The activities of all prepared catalysts for the oxidation of carvacrol and hydrogen peroxide were tested. The performances of all catalysts were compared on the basis of the leaching test results and carvacrol conversions. Thymohydroquinone and benzoquinones were observed as byproducts at high conversions of carvacrol. No product was formed in the absence of a catalyst. Fe(salpn)-NaY catalyst exhibited the highest carvacrol conversion of 27.6% with a yield of 22.0%, followed by Cr(salpn)-NaY catalyst with 23.5% carvacrol conversion and a yield of 17.6%. Other catalysts have shown relatively lower performances in terms of carvacrol conversion and leaching. The Cr(salpn)-NaY catalyst was found to be a more efficient catalyst than others on the basis of leaching and activity tests. With the selected catalyst Cr (salpn)-NaY, the effects of temperature and carvacrol/hydrogen peroxide molar ratio on carvacrol oxidation reactions were investigated. Increasing the temperature from 40 to 60 °C caused an increase in the thymoquinone yield from 6.2% to 16.0%. An increase in carvacrol/hydrogen peroxide molar ratio from 1 to 3 resulted in a decrease in the thymoquinone yield.

Introduction

The development of efficient catalysts for the oxidation of organic compounds under environmentally friendly conditions is an active field of research. Although homogeneous metal-complex catalysts exhibit good activities and selectivities, heterogenization of homogeneous metal-complex catalysts by encapsulating them inside zeolites offers the advantages of both homogeneous and heterogeneous counterparts such easy separation and rigidity.[1] Heterogeneous catalysts can be prepared by using the "ship-in-a-bottle" method.[2] This method involves assembling a metal complex within an intrazeolite space such that the complex, once formed, is too large to diffuse out. If leaching of the zeolite-encapsulated metal complexes does not occur under the reaction conditions, the catalyst is said to be completely heterogeneous. Recently, metal complexes of porphyrins,[3,4] salen,[5] salpn,[1,6] and phthalocyanines[7] have been encapsulated within zeolitic matrixes for the development of efficient oxidation catalysts.

The chemical transformation of abundant and inexpensive products into novel and more valuable compounds can be achieved by liquid-phase oxidation reactions using hydrogen peroxide as a clean oxidant.[8] Hydrogen peroxide is a preferred oxidant because it is easy to handle and its reaction produces only water as a byproduct.[2] Catalytic oxidation of aromatic monoterpenes with hydrogen peroxide is a reaction of industrial

importance.[9] Carvacrol is an example of a *p*-menthane-type aromatic monoterpene, which can be found in the essential oils of several aromatic plants. The catalytic oxidation of carvacrol was expected to give mixture of benzoquinones[11] as shown in eq 1. For the catalytic systems investigated here thymoquinones (TQs), thymohydroquinone (THQs), and other benzoquinones (BQs) appeared successively as reaction products. TQs have a commercial value considerably higher than that of its precursor carvacrol.

Recently, many researchers have pointed out the antitumor and hepatoprotective activity of thymoquinone, as well as its inhibitory effect in membrane lipid peroxidation. Natural sources
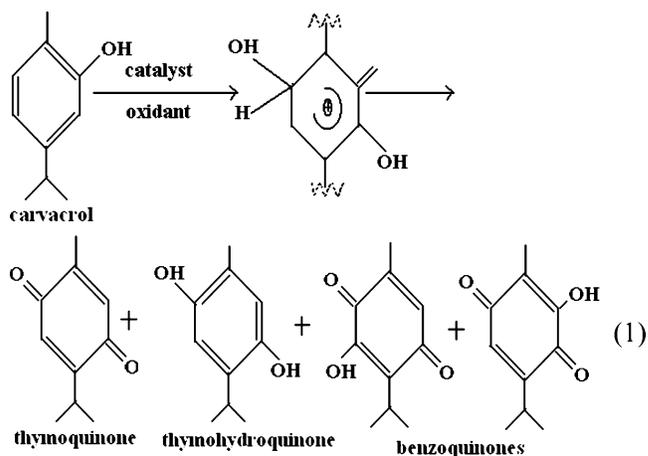
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of thymoquinone are limited to only certain plant resources such as *Nigella sativa* L., *Callitris articulata* (Vahl.) Link., and *Monarda fistulosa* L. Therefore, there is a growing interest in its production by the transformation of other chemicals.[10]

Oregano essential oils rich in carvacrol (47.6%) and thymol (25.1%) were easily oxidized by hydrogen peroxide to oils containing thymoquinone (19.1−63.3%) as the main component in the presence of Fe(III) *meso*-tetraphenylporphyrin or Fe(III) phthalocyanines.[10] The oxidation of carvacrol with hydrogen peroxide has also been studied using Mn(III) porhyrin complexes[8] and Keggin-type tungstoborates.[11] Oxidation of carvacrol by Keggin-type tungstoborates yielded a mixture of benzoquinones containing a small amount of thymoquinone, whereas for Mn(III) porphyrin complexes, oxidation of carvacrol selectively yielded thymoquinone. By using zeolite-encapsulated metal complexes, thymoquinone can be obtained through catalytic oxidation of carvacrol. Oxidation of carvacrol and thymol in the presence of Y-zeolite-entrapped Mn(III) tetra-(4-*N*-benzylpyridyl) porphyrin has been performed.[3] The oxidation of carvacrol (<25% conversion) and thymol (<18% conversion) gave thymoquinone with 100% selectivity. However, leaching of the porphyrin complex from the zeolitic matrix occurred in the presence of H_2O_2 and was accompanied by a partial collapse and changes in the crystalline structure, causing irreversible deactivation.

In this study, zeolite-encapsulated metal (Fe, Cr, Zn, Ni, Bi) complexes are prepared by a general flexible ligand method as described in the literature.[1] *N*,*N*′-bis(salicylidene)propane-1,3-diamine (H2salpn) is used as a flexible ligand. Prepared catalysts are characterized using Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) to confirm the encapsulation of the metal complex. Activities of the catalysts for the decomposition of hydrogen peroxide and oxidation of carvacrol to form thymoquinone are tested. To our knowledge, no previous studies on the oxidation of carvacrol in the presence of metal salpn complexes have been reported. Leaching is the most significant problem for the zeolite-encapsulated metal complexes, so leaching tests or heterogeneity tests were also performed. The screening of the catalysts was carried out on the basis of the leaching test results and catalytic oxidation activities. Because temperature and hydrogen peroxide amount are the most important parameters in oxidation reactions, the effects of temperature and carvacrol-to-hydrogen peroxide molar ratio on the carvacrol oxidation reaction were investigated for only Cr (salpn)-NaY catalyst.

Materials and Methods

Materials. All chemicals and solvents used in the preparation of metal complexes were AR-grade and were used without purification. Metal nitrates [nitrates of Cr(III), Fe(III), Bi(III), Ni(II), and Zn(II)], carvacrol, thymoquinone, salicylaldehyde, 1,3-diaminopropane, and hydrogen peroxide (30 wt % aqueous) were purchased from Sigma-Aldrich. Other reagents and solvents used in HPLC analysis were HPLC-grade and were obtained from Sigma-Aldrich. Zeolite-NaY (CBV100, SiO_2/ Al_2O_3 = 5.1) that contained 13.0 wt % Na_2O was purchased from Zeolyst International Company in the form of powder with sizes of less than 1 μm. The surface area of the zeolite powder was 900 m^2/g. The unit cell formula of this sample was Na_{54}-$(AlO_2)_{54}(SiO_2)_{138}$ when dehydrated. Zeolite-NaY was activated at 500 °C in a static air atmosphere using an oven for 5 h and cooled to room temperature in a desiccator before use.

Catalyst Preparations. H2salpn, metal-exchanged zeolite Y, and encapsulated complexes were prepared by following a procedure similar to one described in the literature.[1]

Preparation of Ligand (H2Salpn). Salicylaldehyde (12.2 g, 0.1 mol) was dissolved in 75 mL of methanol and mixed with a solution of 1,3-diaminopropane (3.75 g, 0.05 mol) in 25 mL of methanol. The mixed solution was refluxed in a water bath for 1 h. After the volume of the solution had been reduced to 50 mL, the flask was kept at ambient temperature for 2 h. Yellow shining plates were filtered, washed with 10 mL of cold methanol, and dried. Finally, the ligand was recrystallized from methanol to give pure product. The melting point of the ligand was found to be 53 °C by differential scanning calorimetric (DSC) analysis using a Shimadzu DSC50 instrument. The run was carried out to a maximum temperature of 600 °C at a 10 °C/min heating rate under a nitrogen flow using 3 mg of sample. The DSC result showed good agreement with the previously reported melting point value of 52 °C.[1]

Preparation of Metal-Exchanged Zeolite Y. NaY zeolite (5 g) was suspended in 300 mL of deionized water containing 0.01 M metal [Cr(III), Fe(III), Bi(III), Ni(II), or Zn(II)] nitrate. The mixture was heated with stirring for 24 h. The solid was filtered, washed with hot distilled water until the filtrate was free of any metal ion content, and then dried for 24 h at 90 °C in air.

Preparation of Encapsulated Complexes. The encapsulated metal complexes were prepared by a general flexible ligand method. In the literature, this method has been described and used by several researchers.[1,5,13] A total of 5 g of metal-exchanged Y zeolite and 10 g of ligand were mixed in a round-bottom flask. The mixture was heated at 100 °C overnight (19 h) in an oil bath with stirring. The ligand was melted at that temperature and acted as a solvent as well as a reactant. The ligand molecule (H2salpn), which was flexible enough to diffuse through the zeolite channels, reacted with the previously ion-exchanged metal ions in the zeolite supercage to obtain the encapsulated metal complexes. The resulting material was removed and Soxhlet extracted with methanol until the complex was free of unreacted excess ligand (at least 72 h). The uncomplexed metal ions present in the zeolite were removed by exchanging them with 0.01 M aqueous NaCl solution for 5 h. The resulting solid was then washed with hot distilled water until no precipitation of AgCl on the reacting filtrate with AgNO3 was observed. The colored solid was dried at 90 °C for 24 h.

Catalyst Characterization. X-ray diffraction (XRD) patterns of the samples were recorded on a Philips X'pert Pro X-ray diffractometer with Cu Kα radiation. Infrared spectra in the region 400−4000 cm^{-1} were recorded from KBr pellets using a Shimadzu 8101 FTIR spectrophotometer. The metal contents in the products were determined using an inductively coupled plasma (ICP) spectrometer (Varian 8410). Catalyst samples for ICP analyses were digested in nitric acid and hydrofluoric acid. Scanning electron micrographs were recorded on a Philips XL 30S FEG instrument. The specific surface area of the zeolite was determined using a Micromeritics ASAP 2010 model static volumetric adsorption instrument using nitrogen at 77 K.

Decomposition of Hydrogen Peroxide. An amount of 0.025 g of encapsulated catalyst was added to an aqueous solution of 30% H_2O_2 (5.5 g, 0.049 mol) at room temperature (25 °C), and the reaction mixture was stirred for the specified time (1 or 2 h). At the end of the reaction, the catalyst was filtered, and the filtrate was diluted to 250 mL with deionized water. Ten milliliters of this solution was withdrawn, and after addition of 20 mL of 2 M H_2SO_4 and 20 mL of deionized water, this sample was titrated against standard 0.2 M KMnO4 solution.

Oxidation of Carvacrol. Carvacrol oxidation was carried out at the specified temperature, with and without catalyst, in a three-necked flask (250 mL) equipped with a magnetic stirrer, a reflux condenser, and a temperature controller. A measured amount of carvacrol (4.4 g, 0.029 mol) and 16 mL of acetonitrile were added successively into the flask. Then, the appropriate amount of 30 wt % aqueous H_2O_2 (0.029 mol) was added for the required carvacrol-to-hydrogen peroxide molar ratio. After the mixture containing carvacrol, acetonitrile, and hydrogen peroxide had been heated to 60 °C, a measured amount of catalyst was added to the reaction mixture, and the reaction was started. The reaction was monitored by taking aliquots at different times. After the samples had been taken from the hot reaction mixture, they were diluted with cold acetonitrile and kept in an ice-water bath, and then they were analyzed by high-performance liquid chromatography (HPLC). The samples were centrifuged to remove the catalyst before analysis. Samples were also taken when there was no catalyst at 60 °C to determine whether the reaction occurs in the absence of catalyst. Because the quinones expected from the reaction mixture undergo facile formation of radicals when exposed to light, immediately after sample collection, vials containing reaction mixture were covered by aluminum foil, to protect them from light.

HPLC analyses were carried out with a method similar to the one described in the literature.[12] An Agilent 1100 HPLC system equipped with a reverse-phase C18 column (250 mm length × 4.6 mm i.d., 5-μm particle sizes, Lichrospher) was used for HPLC analysis. Aliquots of 20 μL were injected, and separation was carried out with an isocratic mobile phase consisting of methanol/water (60:40, v/v) at a flow rate of 1 mL/min and a 30 °C column temperature. The detection wavelengths were 254 nm for detecting carvacrol and thymo-quinone and 294 nm for thymohydroquinone, which has a low absorptivity at 254 nm. These wavelengths were chosen because they gave the maximum absorbance. Prior to injection of a sample, the column was equilibrated with the mobile phase at a flow rate of 1 mL/min for at least 20 min or until a steady baseline was obtained. The percentage of each compound in the reaction mixtures was estimated directly from the corresponding peak area.

Heterogeneity Tests. To test whether the metal complex was leaching from the catalyst, the reaction mixture was filtered hot. The filtration was performed at the reaction temperature in order to prevent the possible readsorption of leached metals. The filtrate was monitored by HPLC analysis to check the progress of the reaction in the homogeneous phase. The heterogeneity of the prepared catalysts was also evaluated by digesting the filtrate after the completion of each reaction. The filtrate was digested in a Teflon beaker by the addition of HNO_3 after all of the organic solvent had completely evaporated. The metal contents of the digested residue for all catalysts were determined using the inductively coupled plasma (ICP) technique. These tests were performed in detail especially the for Cr(salpn)-NaY and Fe(salpn)-NaY catalysts, which exhibited high activities toward carvacrol oxidation.

Results and Discussion

Catalyst Characterization. The color and the metal content of various catalysts, which was estimated by ICP technique, are presented in Table 1. The metal ion contents determined after encapsulation were due to the presence of metal complexes in the zeolite framework. Low metal contents were in good agreement with the results reported earlier in the literature.[1] Catalyst samples preserved their initial color, indicating that

Table 1. Metal Contents of Encapsulated Catalysts

catalyst	metal content (wt %)	color
Cr(salpn)-NaY	1.74	pale blue-green
Fe(salpn)-NaY	1.36	pale brown
Bi(salpn)-NaY	1.04	white
Ni(salpn)-NaY	0.15	off-white
Zn(salpn)-NaY	0.51	off-white

the metal complexes were formed in the zeolite cavities and that the formed complexes were too large to diffuse from the channels of the zeolite.

The prepared catalysts were further characterized using the scanning electron microscopy (SEM), XRD and FTIR techniques to confirm the encapsulation of the metal complexes inside the zeolite supercage.

Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD). SEM was used to observe the morphology of a zeolite after encapsulation of the metal complexes. It was also possible to differentiate complexes present on the external surface from intrazeolite complexes.

The SEM image and the XRD pattern of Cr(salpn)-NaY were similar to those observed for NaY, indicating that they exhibited the same morphologies and crystalline structures, i.e., the framework around the guest molecule Cr(salpn) was faujasite-Y (Figures 1 and 2). The Si/Al ratio of the catalyst samples was 2.5 ± 0.1, ascertained by energy-dispersive X-ray spectroscopy (EDS). It was observed that the Si/Al ratio (2.5 ± 0.1) of the catalyst samples did not change compared to the Si/Al ratio (2.5 ± 0.1) of NaY zeolite. This result confirmed that there was no dealumination of the zeolite. SEM micrographs of NaY and Cr(salpn)-NaY are shown in Figure 1 as a representative case. In the SEM images of catalyst samples, no surface complexes were seen, and the particle boundaries on the external surface of the zeolite were clearly distinguishable. These micrographs reveal the efficiency of purification with Soxhlet extraction for the complete removal of extraneous complexes, leading to well-defined encapsulation in the cavity.[3,14−16]

The XRD patterns of NaY zeolite, M−NaY [M = Ni(II), Zn(II), Cr(III), Fe(III), Bi(III)], and their complexes with H_2salpn (L) encapsulated in NaY zeolite were recorded at 2θ values between 5° and 60°. These observations indicate that the zeolite framework did not undergo any significant structural change during the encapsulation of M−H_2salpn and that the crystallinity of the NaY zeolite was preserved, although a slight change in the intensity of the bands was observed. The slight change in the intensities of the peaks suggests that the supercages of the zeolite were able to store these complexes without any strain.[1,6] The main framework of the zeolite was not damaged. Moreover, no crystalline patterns were seen for the encapsulated complexes; this might be because of their fine distribution in the lattice.[15] All samples exhibited patterns that could be indexed to NaY and not to the complex. This indicates that the crystallinity and morphology of the zeolite were preserved during encapsulation.

XRD can be used to investigate the distribution inside the zeolite matrix. An empirically derived relationship exists between the relative peak intensities of the 331, 311, and 220 reflections and the location of small cations in NaY zeolite.[17] Cations are randomly distributed within the lattice if $I_{331} > I_{220} > I_{311}$. From a comparison of XRD patterns (not shown), it was seen that little change occurred in the relative intensities of the peaks of the 331, 311, and 220 reflections upon encapsulation of metal (Ni, Fe, Zn, Bi) complexes of H_2salpn (L) in zeolite-Y. One can conclude that the zeolite lattice retains its random sodium ion distribution after the process. In contrast,
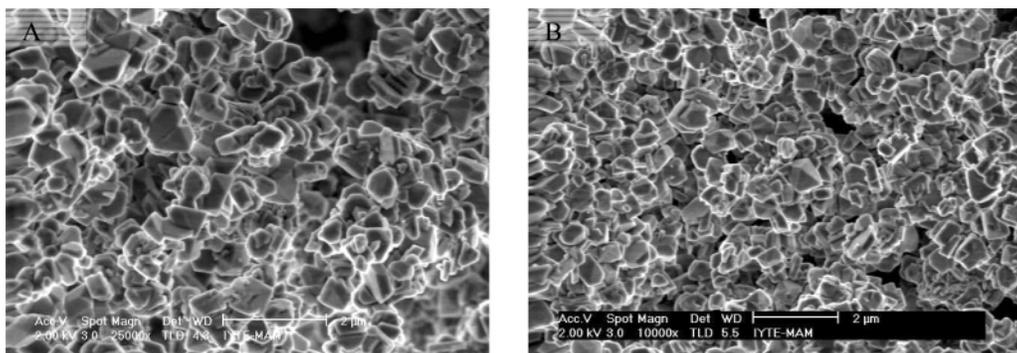
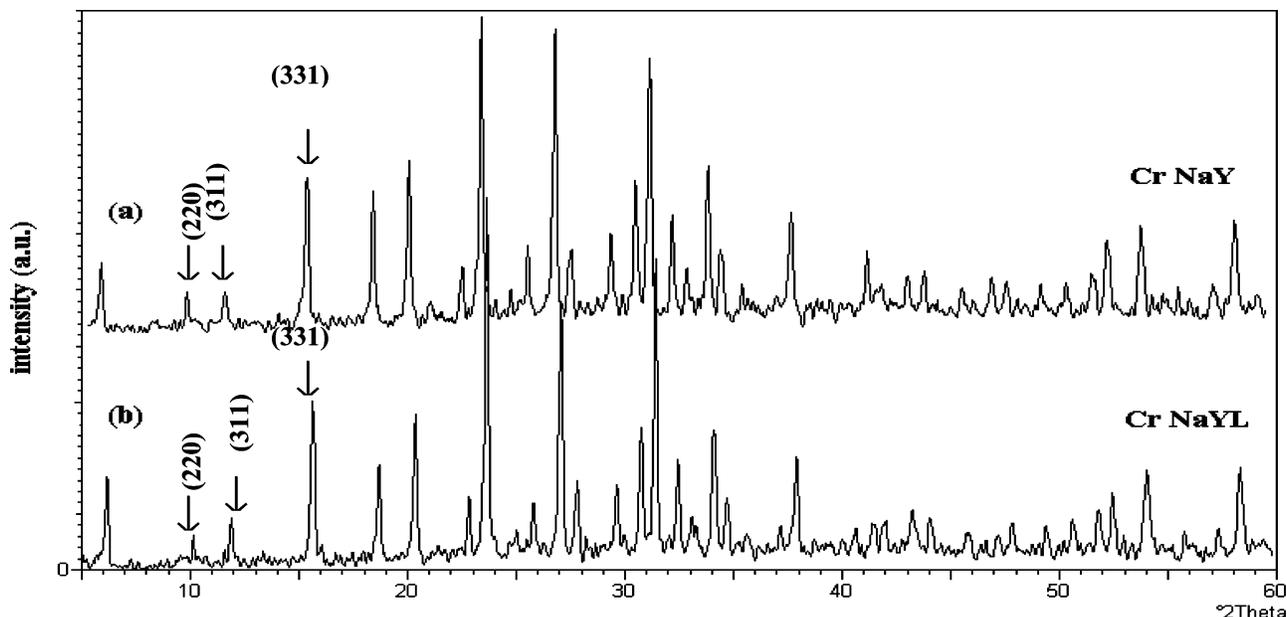**Figure 1.** Scanning electron micrographs of (A) NaY and (B) Cr(salpn)-NaY.

Figure 2. XRD patterns of (a) Cr-NaY (b) Cr(salpn)-NaY.

analysis of the patterns of encapsulated metal complexes indicated that significant cation redistribution occurred following complex formation within the zeolite supercages.[18-20]

The XRD patterns of Cr-NaY and Cr(salpn)-NaY are shown as examples in Figure 2. Those of other catalyst samples were similar. Figure 2 shows that Cr-NaY samples have the faujasite topological structure with high crystallinity. After complexation of the metal ions with the salpn ligand and further Soxhlet extraction, the faujasite structure remained essentially unchanged. This indicates that the complexation and extraction processes did not have strong influence on the structure of the parent Cr-NaY materials. Nevertheless, a slight modification occurred, as confirmed by the alteration of the relative intensities of the 220 and 311 reflections (2θ of about 10° and 12°, respectively). For Cr-NaY, I_{220} was slightly higher than I_{311}, whereas after coordination to salpn, I_{220} became lower than I_{311}. This is typical for the formation of large transition metal complex ions in the supercages of zeolite Y.[18] This can also be verified by FTIR spectroscopy.

FTIR Spectroscopy. IR spectra of NaY zeolite and metal-exchanged zeolites showed strong zeolite lattice bands in the 450−1200 cm^{-1} range. The strong and broad band at ∼1000 cm^{-1} can be attributed to the asymmetric stretching vibrations of (Si/Al)O$_4$ units. The broad bands at 1650 and 3500 cm^{-1} are due to lattice water molecules and surface hydroxyl groups. No shift of the zeolite lattice bands was observed in the spectra of the encapsulated complexes, which further implies that the

Table 2. IR Spectral Data for the Ligand and Its Neat and Encapsulated Complexes

	IR peak (cm^{-1})	
catalyst	ν(C=N)	ν(C=C)
H$_2$ (salpn)	1580	1634
Cr(salpn)-NaY	1525	1626
Cr(salpn)	1531	1616
Fe(salpn)-NaY	1545	1635
Fe(salpn)	1570	1624
Bi(salpn)-NaY	1523	1638
Bi(salpn)	1570	1635
Ni(salpn)-NaY	1523	1639
Ni(salpn)	1546	1632
Zn(salpn)-NaY	1525	1640
Zn(salpn)	1554	1627

zeolite framework remained unchanged upon the encapsulation of the complexes. The coordination in the pores can be identified from the bands observed in the 1200−1600 cm^{-1} region where the zeolite has no bands. However, the bands due to the complexes were weak in intensity because of the low concentrations of the complexes in the lattice.[15]

A partial list of the IR spectra results for the ligand, encapsulated complexes, and free complexes is provided in Table 2. The IR spectrum of the ligand exhibited a broad band between 2400 and 2700 cm^{-1} due to hydrogen bonding between phenolic hydrogens and azomethine nitrogen atoms. The multiple bands around 2900 cm^{-1} in the IR spectrum of the ligand are due to the presence of −CH$_2$− groups. Absence of

Table 3. Percentage Decomposition of Hydrogen Peroxide after 1 and 2 h of Contact Time at Ambient Temperature

	percentage of H_2O_2 reacted	
catalyst	1 h	2 h
Cr(salpn)-NaY	10.4	27.7
Fe(salpn)-NaY	5.9	11.4
Zn(salpn)-NaY	3.2	5.8
Bi(salpn)-NaY	1.8	10.4
Ni(salpn)-NaY	1.2	4.5

the band is due to hydrogen bonding and coordination of oxygen to the metal after proton removal. In the IR spectra of the encapsulated complexes, the zeolite bands were dominant. Only weak bands were observed for zeolite-encapsulated complexes because of the lower complex concentration. The IR spectra of the encapsulated complexes were essentially similar to those of the free complexes. However, some IR bands of encapsulated complexes and free ligand showed some differences from each other. For example, free ligand (H_2salpn) exhibited a ν(C=N) stretch at 1580 cm^{-1}. In complexes, this band shifted to lower frequency. As seen in Table 2, this band appeared in the range 1523−1570 cm^{-1}. This shift is an indication of the coordination of azomethine nitrogen to the metal. Our results showed good agreement with the results previously reported in the litera-ture.[1,21] According to the FTIR results, no significant expansion of the zeolite cavities, dealumination, or structural changes occurred during the encapsulation process. This indicates that the metal complexes fitted nicely within the cavity of the zeolite. The presence of several bands of medium intensity in the 2700−2900 cm^{-1} region indicates the presence of the ethylene group of the amine residue of the ligand.

Decomposition of H_2O_2. Decomposition of hydrogen peroxide was performed over the prepared catalysts to test their catalytic activities. The percentage decomposition of hydrogen was measured at two different reaction times (1 and 2 h), and the relevant data are presented in Table 3. The results show that the decomposition of hydrogen peroxide after 1 h was relatively slow (1.2−5.9%) for Fe-, Zn-, Bi-, and Ni-based catalysts, whereas the Cr-based catalyst showed a decomposition of 10.4%. The hydrogen peroxide decomposition rate was higher for Cr(salpn)-Y and Fe(salpn)-Y catalysts compared to the others. The decomposition of hydrogen peroxide increased for all catalysts even after 2 h. The Cr(salpn)-NaY catalyst was highly active for hydrogen peroxide decomposition. According to the Table 3, the Fe(salpn)-NaY, Cr(salpn)-NaY, Bi(salpn)-NaY catalysts continued to decompose hydrogen peroxide significantly even after 2 h. In the presence of available hydrogen peroxide, the Cr(salpn)-NaY and Fe(salpn)-NaY catalysts were able to decompose hydrogen peroxide effectively, and they were expected to have higher activities toward the oxidation of carvacrol compared to the other catalysts.

Oxidation of Carvacrol. The catalytic activities of the prepared catalysts were evaluated for the oxidation of carvacrol with hydrogen peroxide. Table 4 summarizes the results, i.e., the percentage carvacrol conversion and TQ yield values. It is known that encapsulation of metal ions in zeolites can result in unusual oxidation states/electronic configurations and conse-quent catalytic activity. Hydrogen peroxide has the advantage of high mobility in the pores of zeolite systems because of its small size. Moreover, hydrogen peroxide is inexpensive and sufficiently environmentally friendly. Hydrogen peroxide alone was unable to oxidize carvacrol to a significant extent. With NaY zeolite, no significant carvacrol oxidation was observed, indicating that Y zeolite is inactive under the reaction conditions (Table 4). Oxidation of carvacrol cannot occur unless a catalyst

Table 4. Conversion and Yield in the Oxidation of Carvacrol Reactions[a]

catalyst	carvacrol/H_2O_2 molar ratio	carvacrol conversion[b] (%)	thymoquinone yield[b] (%)
Cr(salpn)-NaY	3	14.2	13.0
Fe(salpn)-NaY	3	12.7	11.6
Zn(salpn)-NaY	3	11.0	11.0
Ni(salpn)-NaY	3	7.9	7.9
Bi(salpn)-NaY	3	3.2	3.2
Cr(salpn)-NaY	1	23.5	17.6
Fe(salpn)-NaY	1	27.6	22.0
Zn(salpn)-NaY	1	6.7	6.7
Ni(salpn)-NaY	1	5.9	5.9
Bi(salpn)-NaY	1	4.9	4.9
NaY	1	no detectable activity[c]	−
none	1	no detectable activity	−

[a] Reaction conditions: acetonitrile as the solvent, 60 °C, 5 h, 0.1 g of catalyst. [b] Conversion and yield were determined by HPLC. Conversion of reactant can be calculated as $\{[(\text{reactant})_{in} - (\text{reactant})_{out}]/(\text{reactant})_{in}\} \times 100$. Yield for a specific product can be calculated as $[\text{product}/(\text{reactant})_{in}] \times 100$. [c] NaY showed no catalytic activity toward oxidation of carvacrol.
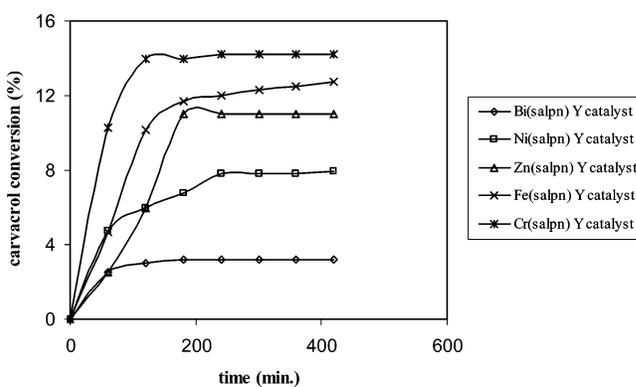
Figure 3. Percentage carvacrol conversion (reaction conditions: carvacrol/H_2O_2 molar ratio = 3, 0.1 g of catalyst, 60 °C).
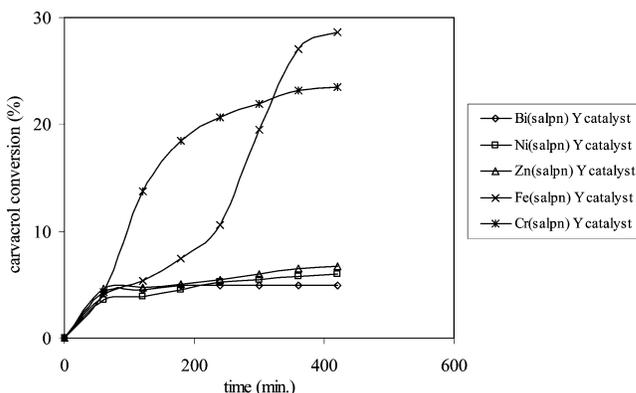
Figure 4. Percentage carvacrol conversion (reaction conditions: carvacrol/H_2O_2 molar ratio = 1, 0.1 g of catalyst, 60 °C).

promotes the reaction. This observation is in agreement with the observations made by several researchers.[3,15] To determine the performances of the catalysts, the percentage carvacrol conversion was plotted as a function of time at two different carvacrol-to-hydrogen peroxide molar ratios. The results of the carvacrol oxidation reactions at carvacrol-to-hydrogen peroxide molar ratios of 3 and 1 are seen in Figures 3 and 4, respectively. As seen from these figures, all catalysts exhibit activity for the oxidation of carvacrol. A mixture of thymoquinones (TQs), thymohydroquinone (THQs), and other benzoquinones (BQs) was obtained from the oxidation of carvacrol. No attempts were made to identify the THQs and BQs.

At a carvacrol-to-hydrogen peroxide molar ratio of 3, carvacrol conversions of 11.0%, 7.9%, and 3.2% were deter-

mined for Zn(salpn)-NaY, Ni(salpn)-NaY, and Bi(salpn)-NaY catalysts, with close to 100% selectivity (Table 4). Despite the low carvacrol conversions, the Bi-, Ni-, and Zn-based catalysts gave close to 100% selectivities for thymoquinone formation. Minor products (THQs and BQs) were detected only at higher conversions. Among the prepared catalysts, Cr(salpn)-NaY performed best and gave the highest carvacrol conversion of 14.2%, whereas Fe(salpn)-NaY provided a carvacrol conversion of 12.7%. In terms of the formation of thymoquinones, a maximum of 13.0% thymoquinone formation was obtained with the Cr-based catalyst, which was followed by the Fe-, Zn-, Ni-, and Bi-based catalysts in decreasing order.

As stated above, despite the low carvacrol conversions, the Bi-, Ni-, and Zn-based catalysts gave close to 100% selectivities for thymoquinone formation. At the reaction condition used here in the oxidation of carvacrol, these catalysts exhibited aromatic-ring-oxidation activity, producing thymoquinones as the only major product (100% selectivity). Minor products, if any, were not detected by HPLC under the reaction conditions used. According to the literature, quinones can result from the oxidation of a hydroquinone intermediate.[8,10,11,22] The formation of TQs from carvacrol is a result of the selective hydroxylation of the aromatic ring in the para position relative to the OH group, followed by the subsequent oxidation of the resulting hydroquinone to the quinone stage.[8] This hydroquinone derivative might arise from a protonated intermediate, the *p*-hydroxylated species. Such an intermediate is stabilized by the OH present in carvacrol (eq 1).[8]

With the Cr-based catalyst, a 13% TQ yield was observed, along with small amounts of THQs and BQs. On the other hand, using the Fe-based catalyst, TQ formation was found to be 11.6% with a small amount of THQs. The Zn, Ni, and Bi catalysts were more selective for TQ formation than the Fe- and Cr-based catalysts. However, leached metal ions detected by the ICP technique in the reaction medium catalyzed the carvacrol oxidation reaction homogeneously. Therefore, it was difficult to call these catalysts complete heterogeneous catalysts because of significant metal ion leaching from the catalysts into the reaction medium. For the Zn, Ni, Bi, and Fe catalysts, the presence of metal ions in the reaction mixture after 5 h was detected by ICP analysis. The percentages of leached metal ions were 25.2%, 19%, 64%, and 10% for the Zn, Ni, Bi, and Fe catalysts, respectively (reaction conditions: carvacrol/H_2O_2 molar ratio = 3, 0.1 g catalyst, 60 °C). For the Cr catalyst, no metal ion was detected by the ICP technique. Because the Cr- and Fe-based catalysts exhibited better catalytic activity than the others, we decided to further examine the heterogeneities of these catalysts by the hot filtration technique, and the results are presented later in the text. As seen from Figure 3, the conversion of carvacrol increased with time for all catalysts, but reached a steady state at different times. The maximum conversion of about 14.2% was observed with Cr(salpn)-NaY after a period of 1.5 h. For Fe(salpn)-NaY, a 12.7% carvacrol conversion was observed within 2 h. The rest of the catalysts provided lower conversions than the Fe(salpn)-NaY and Cr(salpn)-NaY catalysts.

As seen from Table 4, the maximum conversions were achieved using the Cr(salpn)-NaY and Fe(salpn)-NaY catalysts for both carvacrol-to-hydrogen peroxide molar ratios of 3 and 1. When the carvacrol-to-hydrogen peroxide molar ratio was decreased to 1 (i.e., hydrogen peroxide was increased) again, the oxidation of carvacrol gave thymoquinones with 100% selectivity for the Zn, Ni, and Bi catalysts. The selectivity toward thymoquinone decreased with increasing carvacrol conversion

for the Fe(salpn)-NaY and Cr(salpn)-NaY catalysts. The decrease in selectivity was due to two additional components observed in the reaction mixture, and no attempts were made to identify them. These were probably higher-molecular-weight compounds formed in the reaction mixture through the association of thymoquinones, as thymoquinones have a tendency to polymerize.

For the Fe(salpn)-NaY catalyst, the carvacrol conversion was much higher than that obtained for the other catalysts, as seen in Figure 4. This increase in carvacrol conversion can be explained by the hydrogen peroxide decomposition data. According to these data, the Fe(salpn)-NaY catalyst reached equilibrium in a longer time. The Fe-based catalyst exhibited a good activity, and the carvacrol conversion increased from 12.7% to 27.6% after the hydrogen peroxide amount was increased. The reaction continued with more available hydrogen peroxide. The carvacrol conversion increased from 14.2% to 23.5% for the Cr(salpn)-NaY catalyst after the hydrogen peroxide amount was increased. The Zn- and Ni-based catalysts, as well as the Bi-based catalyst (4.9%), exhibited smaller conversion values of 6.75% and 5.9%, respectively, compared to when the carvacrol-to-hydrogen peroxide ratio was 3.

In the literature, the oxidation of carvacrol with hydrogen peroxide has been studied by using Mn(III) porphyrin complexes,[8] Fe(III) *meso*-tetraphenylporphyrin or Fe(III) phthalocyanines,[10] and Keggin-type tungstoborates[11] under homogeneous conditions. Mn(III) porphyrin complexes exhibit high carvacrol conversions with a selectivity range of 70−99.6%. Oregano essential oils containing mainly 47.6% thymol and 25.1% carvacrol were transformed to oils containing thymoquinones (20−66%) using Fe(III) *meso*-tetraphenylporphyrin or Fe(III) phthalocyanine complexes.[10] Keggin-type tungstoborates showed carvacrol conversion values of 35−40%, providing mainly mixtures of benzoquinones, with a small amount (2.5%) of TQs.[11] With heterogeneous zeolite-encapsulated Mn(III) tetraporphyrin complex catalysts, the oxidation of carvacrol (<25% conversion) formed thymoquinones with 100% selectivity. However, leaching of the porphyrin from Mn(III) porphyrin-NaY and changes in its crystalline structure occurred.[3] In this study, high carvacrol conversions of up to 85% with high selectivites (76.8−100%) toward thymoquinone formation were observed.

To test whether the metal complex was leaching from the catalyst, the reaction mixture was filtered hot. The leaching of the active species from the heterogeneous catalysts into the solution is an important issue for identifying whether the reaction takes place homogeneously or heterogeneously. The catalysts were filtered off during the oxidation process, and the carvacrol was monitored in the filtrate by HPLC. This test was performed in detail for the Cr(salpn)-NaY and Fe(salpn)-NaY catalysts, which showed good carvacrol oxidation performances. Time vs conversion curves with catalyst and after filtering off the catalyst are presented in Figure 5.

No further reaction was noted after catalyst removal for Cr(salpn)-NaY, as seen in Figure 5. However, when the Fe(salpn)-NaY catalyst was removed from the reaction mixture, the conversion decreased but continued. It is clear that the heterogeneity of the Cr-based catalyst was better than that of the Fe-based catalyst. The leaching of metals can be attributed to the negative effect of hydrogen peroxide on the stability of the encapsulated metal complexes. The chromium complex when immobilized seemed to be more stable than the iron complex in the oxidizing medium. In this research, the XRD patterns and SEM micrographs of all catalysts were recorded after each
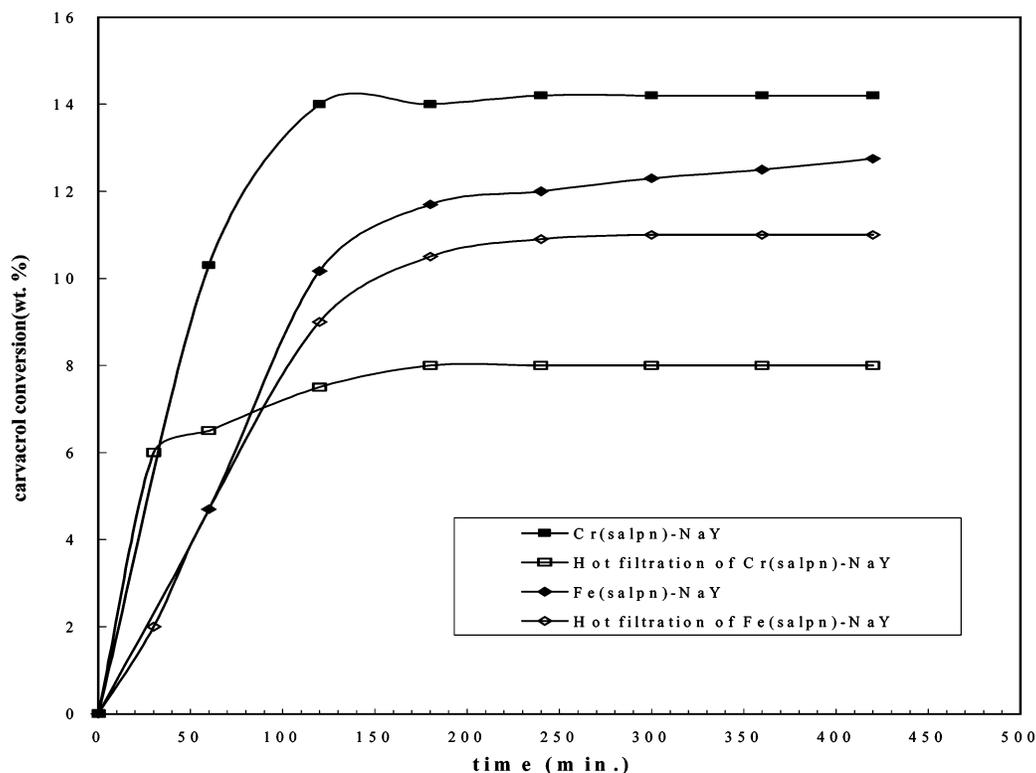
Figure 5. Percentage carvacrol conversion (reaction conditions: carvacrol/H_2O_2 molar ratio = 3, 0.1 g of catalyst, 60 °C, hot filtration after 30 min).

Table 5. Oxidation of Carvacrol by Cr(salpn)-NaY Catalyst under Different Reaction Conditions[a]

temperature (°C)	carvacrol/H_2O_2 molar ratio	conversion[b] (%)	TQ yield[b] (%)
	Effect of Temperature		
25	2	none	−
40	2	6.2	6.2
50	2	18.0	16.0
60	2	19.2	15.0
	Effect of Carvacrol/H_2O_2 Molar Ratio		
50	3	3.7	3.7
50	2	18.0	16.0
50	1	27.0	23.0

[a] Reaction conditions: acetonitrile as the solvent, 5-h reaction time, 0.13 g of Cr(salpn)-NaY catalyst. [b] Conversion and yield were determined by HPLC. Conversion of reactant can be calculated as {[(reactant)$_{in}$ − (reactant)$_{out}$]/(reactant)$_{in}$} × 100. Yield for a specific product can be calculated as [product/(reactant)$_{in}$] × 100.

step of preparation and after the reaction. No significant loss of crystallinity was observed.

The Cr(salpn)-NaY catalyst was selected for a recycling study because of its high activity and heterogeneity. The catalyst was separated from the reaction mixture after each experiment by filtration, washed with solvent, and dried. Catalyst was recycled at least 3 times without a significant change in the catalytic activity. In addition, the comparable IR spectral patterns of fresh and used encapsulated chromium-based catalysts suggested that this catalyst could be used further for catalytic study.

Effect of Temperature. Four different temperatures (25, 40, 50, and 60 °C) were used while other parameters (i.e., catalyst weight, carvacrol/H_2O_2 molar ratio) were kept fixed. The results are presented in Table 5. At 25 °C, no carvacrol conversion was observed. At 50 and 60 °C, 16% and 15% TQ yields were observed, along with small amounts of THQ and BQ derivatives. At low temperatures (e.g., 40 °C), reactions were more selective for TQ formation compared to high temperatures. However, in these reactions, the conversions were as low as 6.2%.

Effect of Carvacrol/Hydrogen Peroxide Molar Ratio. The effect of the hydrogen peroxide concentration on the percentage carvacrol conversion as a function of reaction time was also studied. The carvacrol/H_2O_2 molar ratios used were 1, 2, and 3, and the amount of carvacrol was kept constant with the other remaining parameters.

The percentage carvacrol conversion was found to increase with decreasing carvacrol/H_2O_2 molar ratio, i.e., increasing H_2O_2 amount (Table 5). However, by increasing the H_2O_2 amount, the system attained a steady state after a certain time. When the conversion was increased by decreasing the carvacrol/H_2O_2 molar ratio, a higher TQ (23% yield) amount was observed, along with small amounts of THQ and BQ derivatives. For lower conversions, the reactions were more selective for TQ formation compared to higher conversions.

Conclusions

NaY zeolite-encapsulated Ni (II), Zn(II), Bi(III), Fe(III), and Cr(III) complexes of H_2salpn ligand were prepared using a flexible ligand method. The characterization results obtained by XRD, SEM, and FTIR spectroscopy confirmed the encapsulation of the metal complexes in the supercages of the NaY zeolite. All of the NaY zeolite-encapsulated complexes were active catalysts for the decomposition of hydrogen peroxide and for the oxidation of carvacrol to thymoquinone with good selectivity. Thymoquinones, compounds with a commercial value considerably higher than those of their precursors, can be easily obtained by using zeolite-encapsulated metal(salpn) catalysts. Cr(salpn)-NaY showed a remarkable performance in terms of activity toward carvacrol oxidation reaction and heterogeneity.

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